Supporting Information Available

Proof of Eq. 4

Here we summarize the proof of Eq. 4 as derived in reference.[22] With y_i and y_j denoting a pair of the (q,p) phase space coordinates, the ensemble average of the function $f(q,p) = y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j}$ is

$$\left\langle y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} \right\rangle \overset{3}{=} \frac{1}{h^n \mathcal{Z}(\mathbf{T})} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_n \int_{-\alpha_1}^{\gamma_1} dq_1 \cdots \int_{-\alpha_n}^{\gamma_n} dq_n \; y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} e^{-\mathcal{H}(q,p)/\mathbf{kT}}$$

Using the fact that

$$\frac{\partial e^{-\mathcal{H}(q,p)/\mathbf{kT}}}{\partial y_j} = -\frac{1}{\mathbf{kT}} \frac{\partial \mathcal{H}(q,p)}{\partial y_j} e^{-\mathcal{H}(q,p)/\mathbf{kT}}$$

we obtain

$$\left\langle y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} \right\rangle = -\frac{\mathbf{kT}}{h^n \mathcal{Z}(\mathbf{T})} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_n \int_{-\alpha_1}^{\gamma_1} dq_1 \cdots \int_{-\alpha_n}^{\gamma_n} dq_n \; y_i \frac{\partial e^{-\mathcal{H}(q,p)/\mathbf{kT}}}{\partial y_j}$$

Applying the integration by parts relationship

$$\int u dv = uv - \int v du$$

for the y_j coordinate to the expression on the right leads to

$$\begin{aligned} \left\langle y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} \right\rangle = &-\left[\frac{\mathbf{kT}}{h^n \mathcal{Z}(\mathbf{T})} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_n \int_{-\alpha_1}^{\gamma_1} dq_1 \cdots \int_{-\alpha_n}^{\gamma_n} dq_n \; y_i e^{-\mathcal{H}(q,p)/\mathbf{kT}} \right]_{min(y_j)}^{max(y_j)} \\ &+ \frac{\mathbf{kT}}{h^n \mathcal{Z}(\mathbf{T})} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_n \int_{-\alpha_1}^{\gamma_1} dq_1 \cdots \int_{-\alpha_n}^{\gamma_n} dq_n \; \frac{\partial y_i}{\partial y_j} e^{-\mathcal{H}(q,p)/\mathbf{kT}} \end{aligned}$$

In the first term on the right, the integration with respect to y_j is replaced with evaluation at the limits of integration of the y_j coordinate. Clearly

$$\frac{\partial y_i}{\partial y_j} = \delta_{i=j}$$

Moreover, if we assume that the Hamiltonian is such that it either vanishes at the limits of y_j, or has the same value (possibly infinity) at the limits, then the first term on the right vanishes. This assumption on the Hamiltonian holds for most cases, with the Hamiltonian typically vanishing when y_j is a configuration coordinate, and being positive infinity for momentum coordinates. With this assumption

$$\left\langle y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} \right\rangle = \frac{\mathbf{kT}}{h^n \mathcal{Z}(\mathbf{T})} \int_{-\infty}^{\infty} dp_1 \cdots \int_{-\infty}^{\infty} dp_n \int_{-\alpha_1}^{\gamma_1} dq_1 \cdots \int_{-\alpha_n}^{\gamma_n} dq_n \, \delta_{i=j} e^{-\mathcal{H}(q,p)/\mathbf{kT}}$$

When $i \neq j$, $\delta_{i=j} = 0$ and the term on the right is zero. When $i = j$, $\delta_{i=j} = 1$, and the integral term is simply $h^n \mathcal{Z}(\mathbf{T})$ from Eq. 2. Hence

$$\left\langle y_i \frac{\partial \mathcal{H}(q,p)}{\partial y_j} \right\rangle = \mathbf{kT} \delta_{i=j}$$

This establishes the equipartition relationship in Eq. 4.

This material is available free of charge via the Internet at `http://pubs.acs.org`.